

# Bifunctional Electrolytes for Lithium-ion Batteries

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ES068

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# Overview

## Timeline

- **Start Date:** April 2009
- **End Date:** May 2013
- **Percent Complete:** 50%

## Budget

- **Total Project Funding** \$798K
- **FY09** - \$199.5 K
- **FY10** - \$199.7 K
- **FY11** - \$199.7 K

## Barriers

- Abuse Tolerance

## Partners

**Novolyte Technologies**

Independence, OH

**The Lubrizol Corporation**

Wickliffe, OH

**University of Dayton**

Dayton, OH

# Objectives

- Design, synthesize, and characterize novel lithium salts containing functionalized boron and phosphorus moieties known to impart materials with flame retardant properties Flame Retardant Ions (FRLons) to improve safety of lithium ion batteries.
- Assess physical and electrochemical characteristics of FRLons.
- Gain insight into the reactivity of these novel bifunctional electrolytes toward lithium ion charged anodes using a combination of electrochemical and *in situ* spectroscopic techniques.
- Develop structure-function relationships that will guide further search of optimized FRLons and other species that contribute to enhance abuse tolerance.

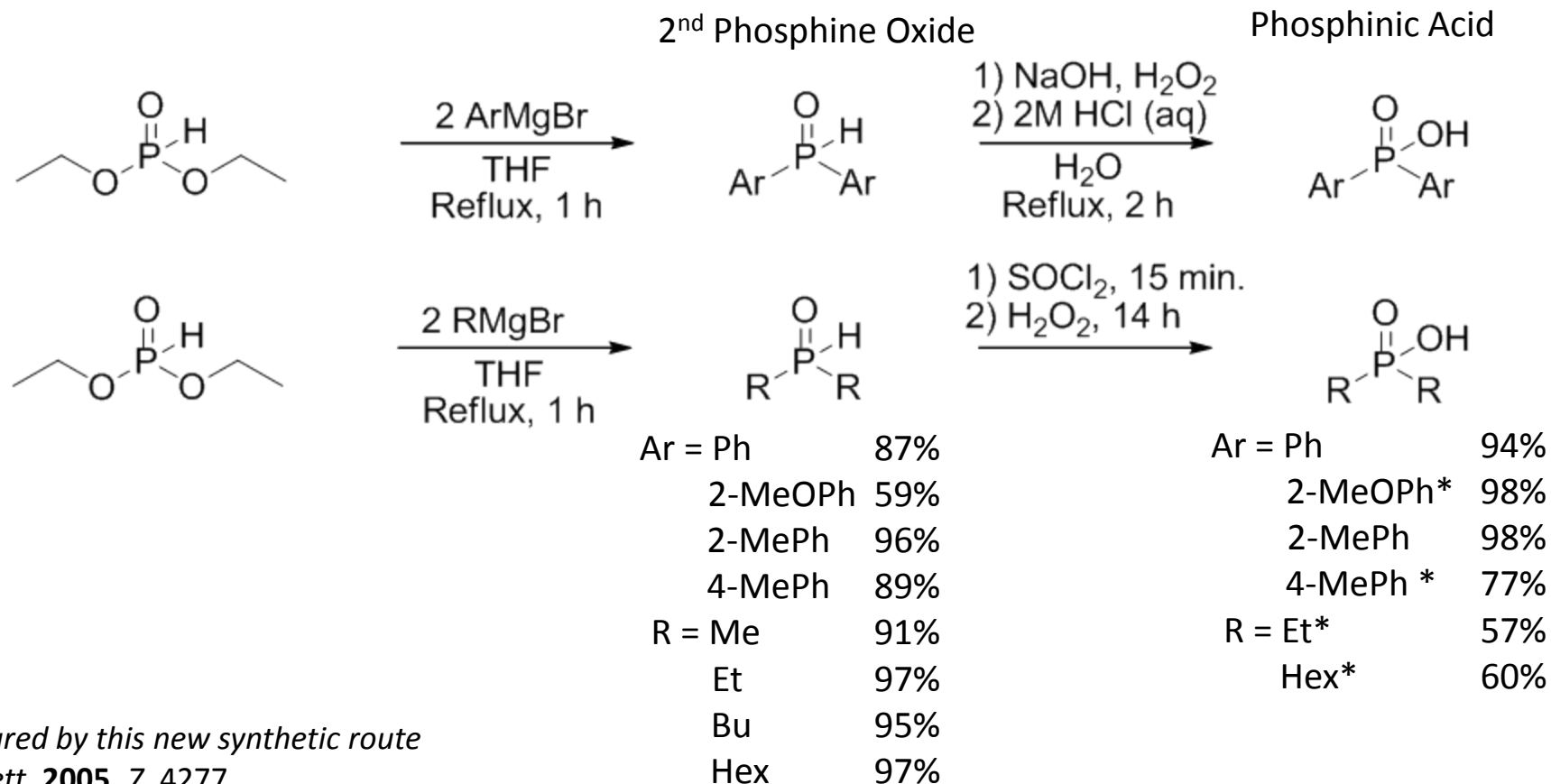
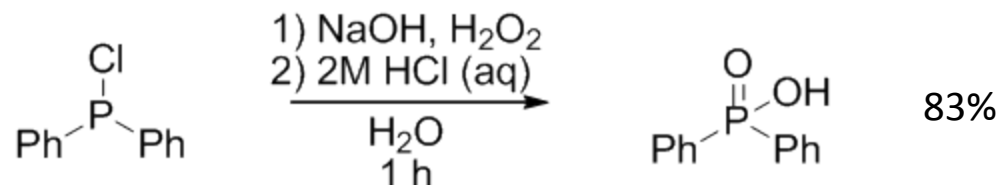
# Summary of Milestones

Month/Year	Milestones
Dec-09	<ul style="list-style-type: none"> <li>▪ Synthesize first generation <u>F</u>lame <u>R</u>etardant <u>I</u>ons (FRLons)</li> <li>▪ Complete design of spectroelectrochemical cell for in situ Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) for measurements involving highly reactive Li-based systems.</li> <li>▪ Initiate contacts with Novolyte Technologies to undertake testing of materials developed at Case in actual coin cells.</li> </ul>
Apr-10	<ul style="list-style-type: none"> <li>▪ Complete full characterization of first FRLon including preliminary charge-discharge curves in actual coin cells.</li> <li>▪ Complete construction of in situ ATR-FTIR cell.</li> </ul>
Nov-10	<ul style="list-style-type: none"> <li>▪ Publish paper on first FRLon</li> <li>▪ Synthesize and <i>fully</i> characterize second generation FRLons</li> </ul>
Apr-11	<ul style="list-style-type: none"> <li>▪ Initiate <i>in situ</i> spectroscopic and impedance measurements with the second generation FRLons.</li> <li>▪ Synthesize and <i>fully</i> characterize third generation FRLons</li> </ul>
Nov-11	<ul style="list-style-type: none"> <li>▪ Submit second paper on FRLons including electrochemical and flame retardant properties</li> <li>▪ Optimize design of advanced cell for ATR-FTIR</li> </ul>
Apr-12	<ul style="list-style-type: none"> <li>▪ Synthesize and <i>fully</i> characterize fourth generation FRLons</li> <li>▪ Complete acquisition and analysis of ATR-FTIR and impedance measurements with all generations of FRLons prepared under this program</li> </ul>

# Approach/Strategy

- Incorporate flame retardant chemical groups to anionic species that display good transport properties and use these materials as alternative lithium salts or as additives to more conventional electrolytes.
- Gain insight into modifications to the structural and physicochemical properties of the passive on lithium ion anodes induced by the FRLs using a combination of attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and conventional electrochemical techniques including impedance spectroscopy.
- Build up knowledge base that will afford rational guidelines for the search of novel materials displaying required properties to enhance abuse tolerance of high energy density, high power density lithium ion batteries.

# Syntheses of FRlon Precursors

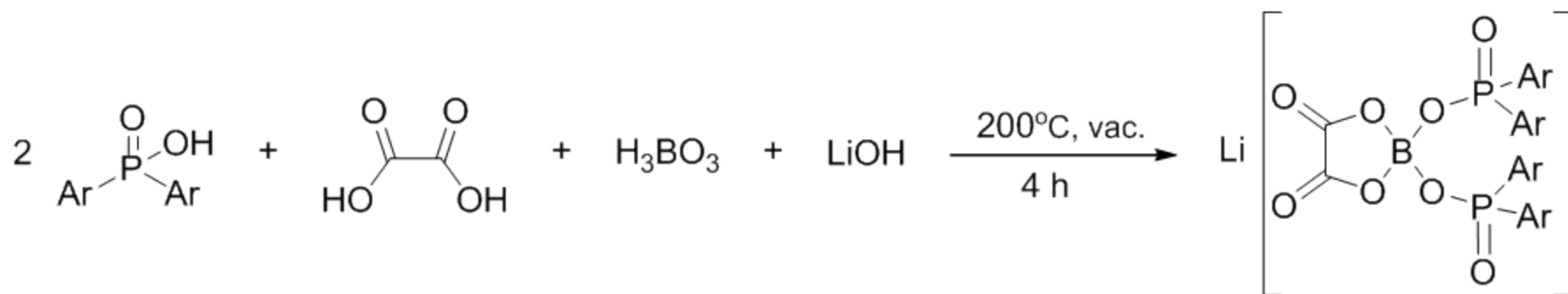


\*Prepared by this new synthetic route

Org. Lett. **2005**, 7, 4277.

Eur. J. Org. Chem. **2003**, 4216.

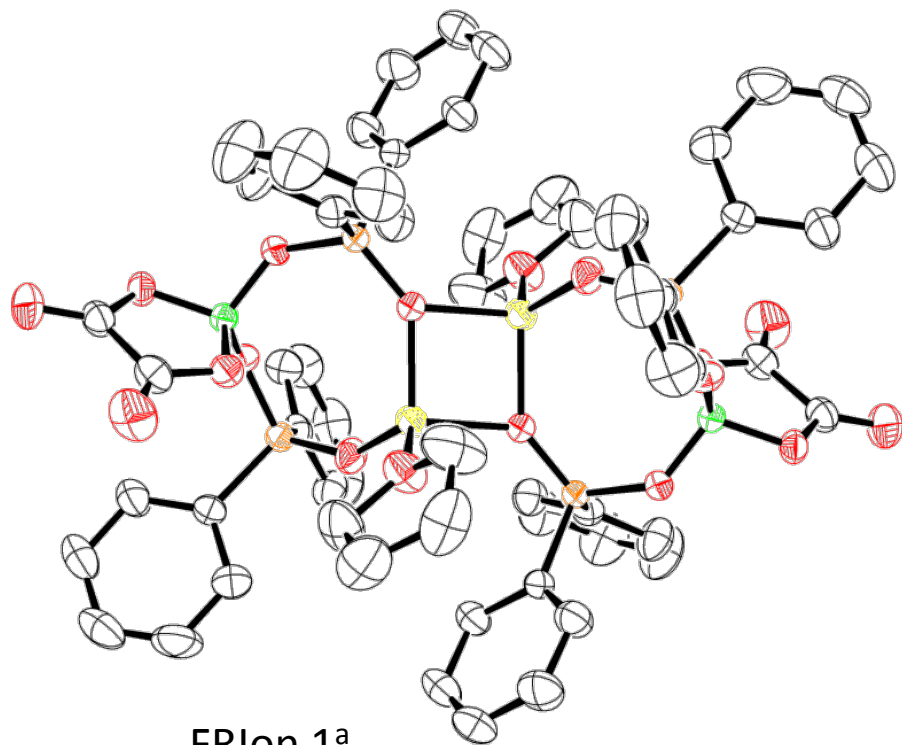
# Synthesis of FRlons



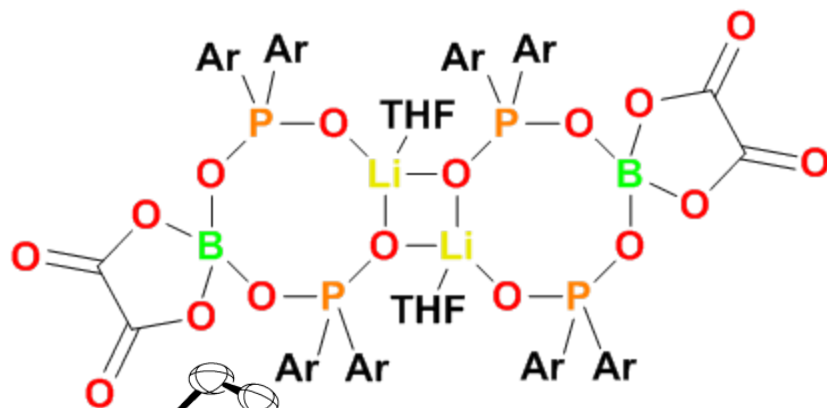
	Ar	<sup>31</sup> P NMR Shift <sup>a,b</sup> (ppm)	<sup>11</sup> B NMR Shift <sup>a,c</sup> (ppm)	m.p. <sup>d</sup> (°C)	Description
FRlon 1	Ph	20.9	-16.5	161-166	Hygroscopic colorless crystals
FRlon 2	2-MePh	21.1	-15.8	175-180	Hygroscopic colorless crystals

<sup>a</sup>NMR Solvent was DMSO. <sup>b</sup>Externally referenced to 85% H<sub>3</sub>PO<sub>4</sub>. <sup>c</sup>Externally referenced to H<sub>3</sub>BO<sub>3</sub>. <sup>d</sup>Uncorrected.

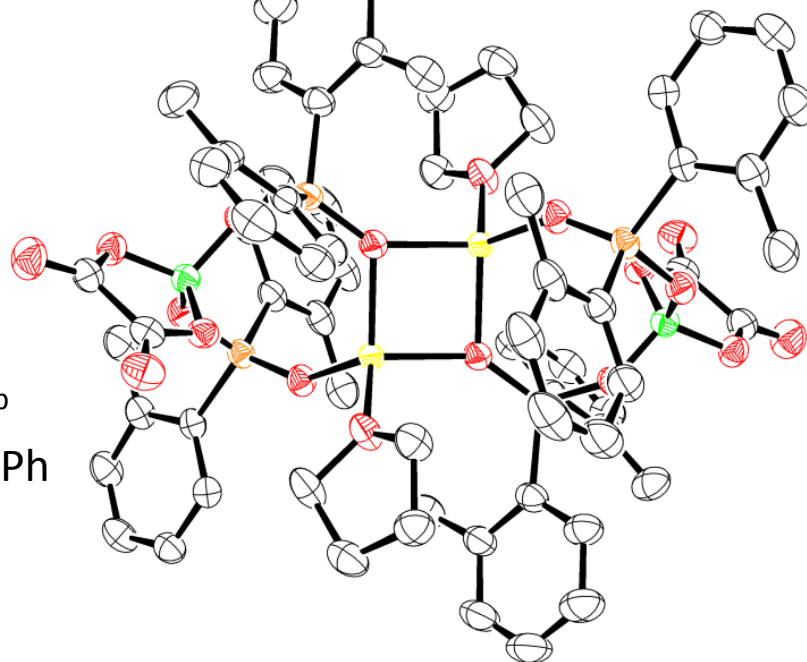
# Structural Characterization of FRlons



FRlon 1<sup>a</sup>  
Ar = Ph



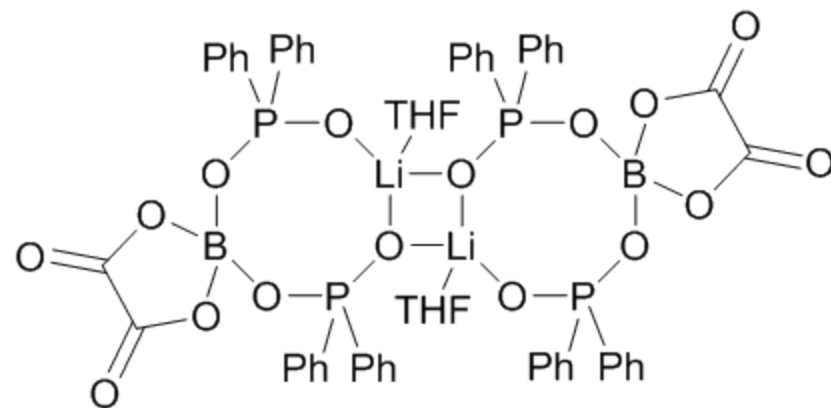
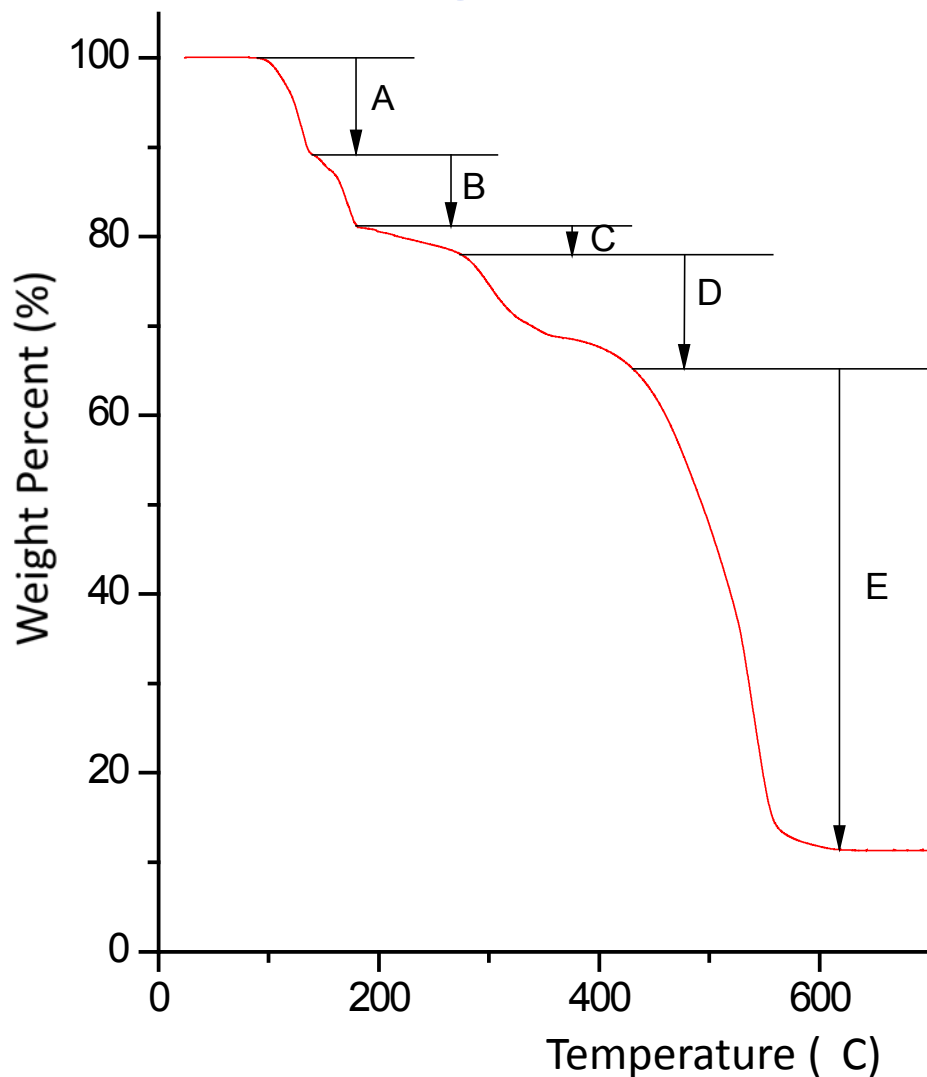
FRlon 2<sup>b</sup>  
Ar = 2-MePh



<sup>a</sup>Shaffer, A. R., Deligonul, N., Scherson, D. A., Protasiewicz, J. D. *Inorg. Chem.* **2010**, 49, 10756-10758.

<sup>b</sup>Manuscript in preparation

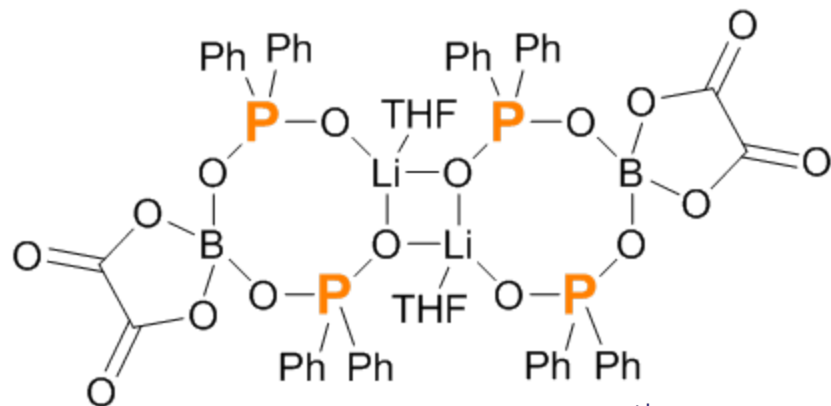
# Thermogravimetric Analysis of FRlon 1



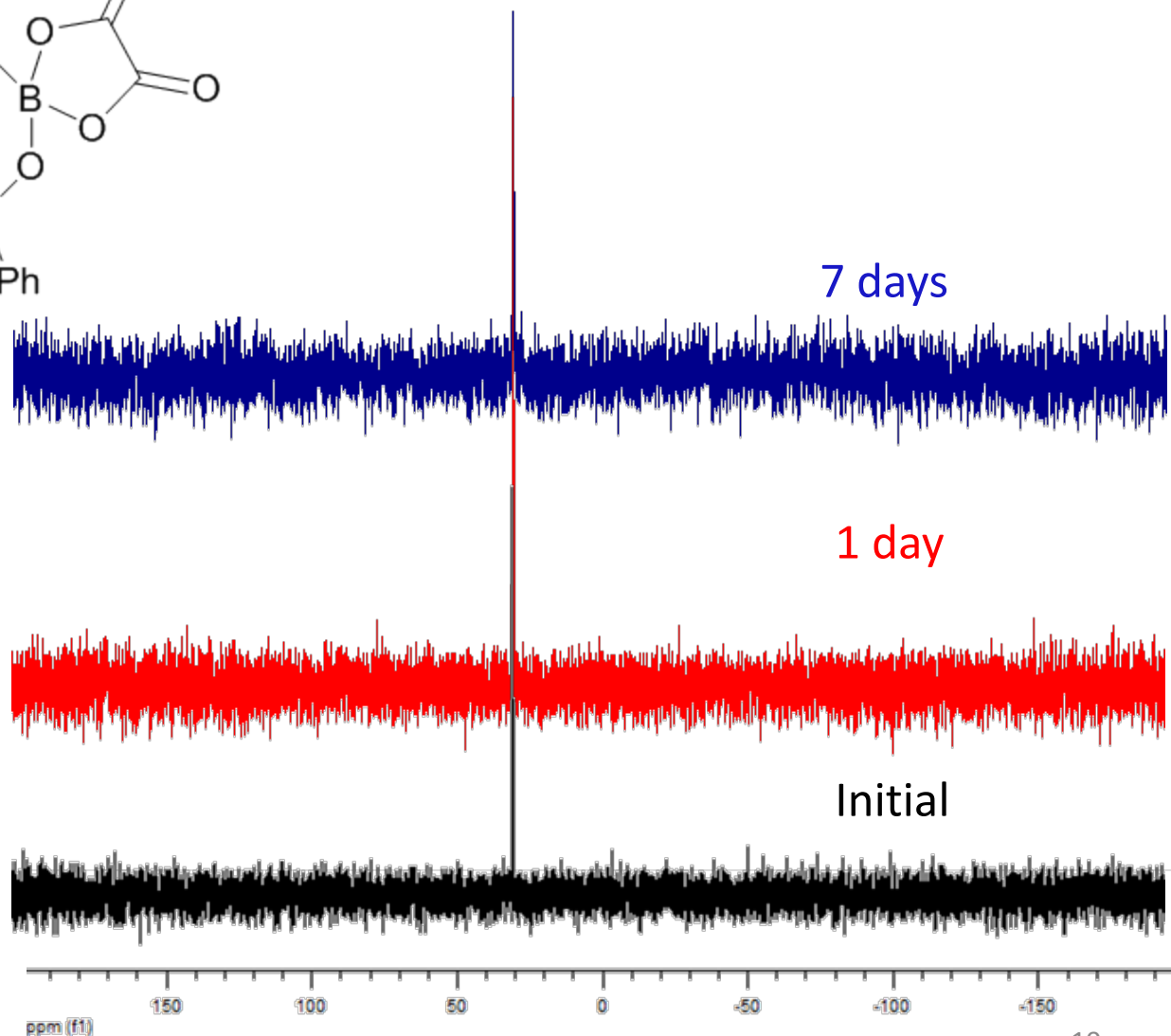
Event	T (°C)	Possible Fragment Loss
A	94.5	2 THF
B	155.4	2 CO <sub>2</sub>
C	179.2	CO <sub>2</sub>
D	249.5	THF, CO <sub>2</sub>
E	343.6	Unknown

FRlon 1 is stable up to temperatures slightly higher than 150°C.

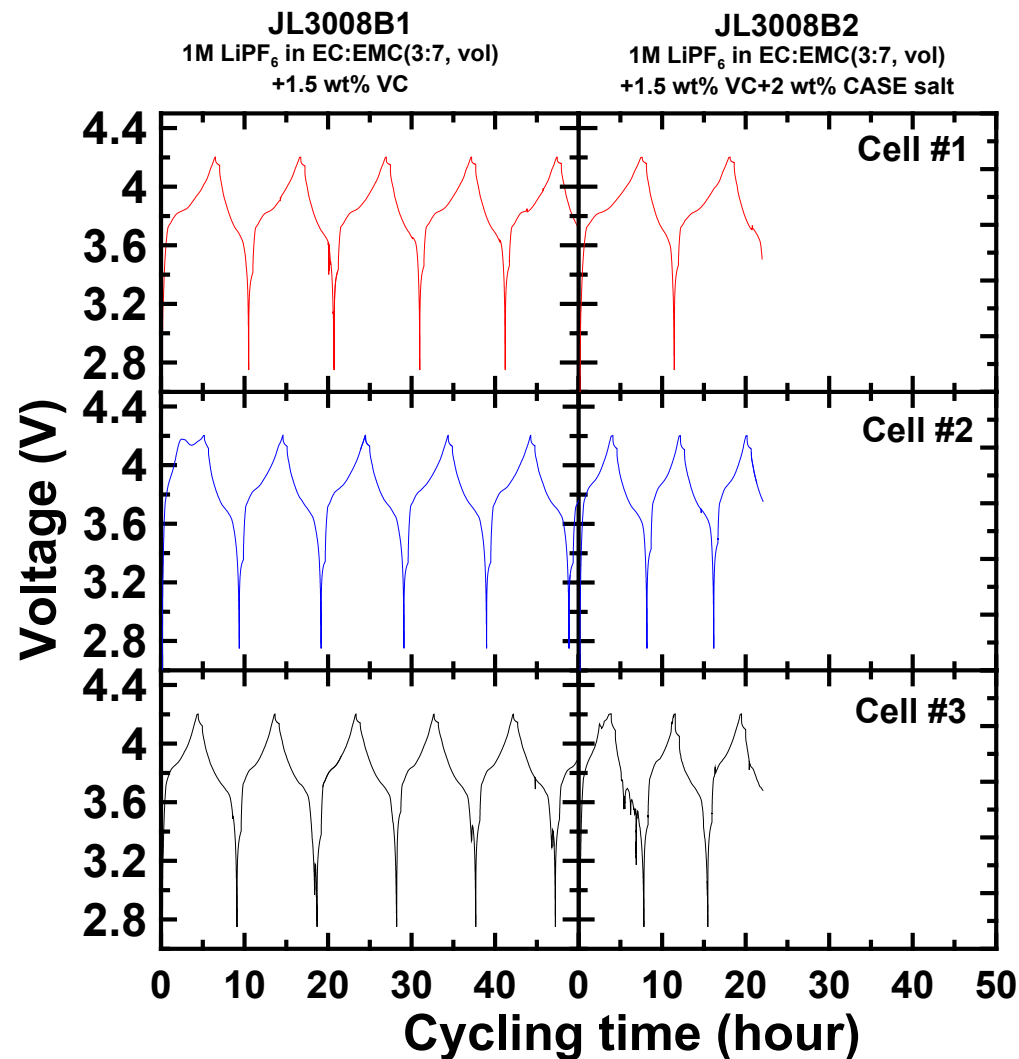
# Thermal Stability of FRlon 1 in PC



FRlon 1 in propylene carbonate (PC) was heated in a sealed J-Young NMR tube to 70 °C for 1 week and monitored via  $^{31}\text{P}$  NMR spectroscopy (singlet at 25.8 ppm) using a 400 MHz NMR spectrometer. After one week, no decomposition products were detected.

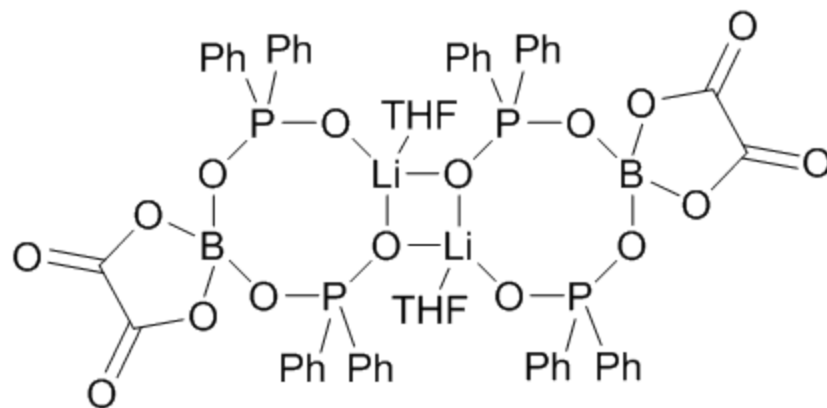


# Preliminary Charge/Discharge Curves



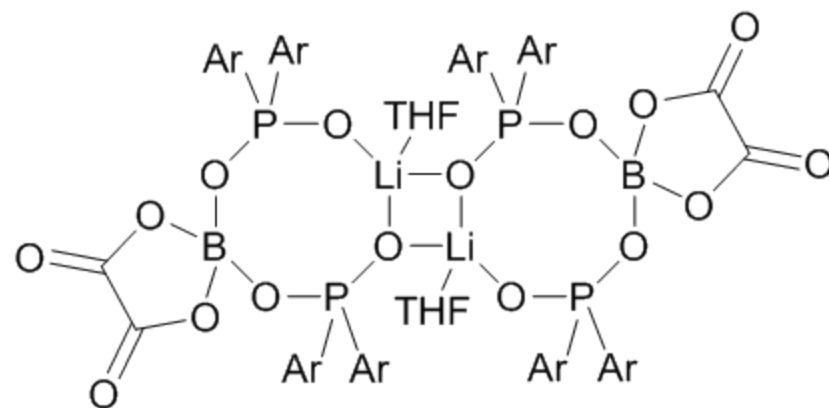
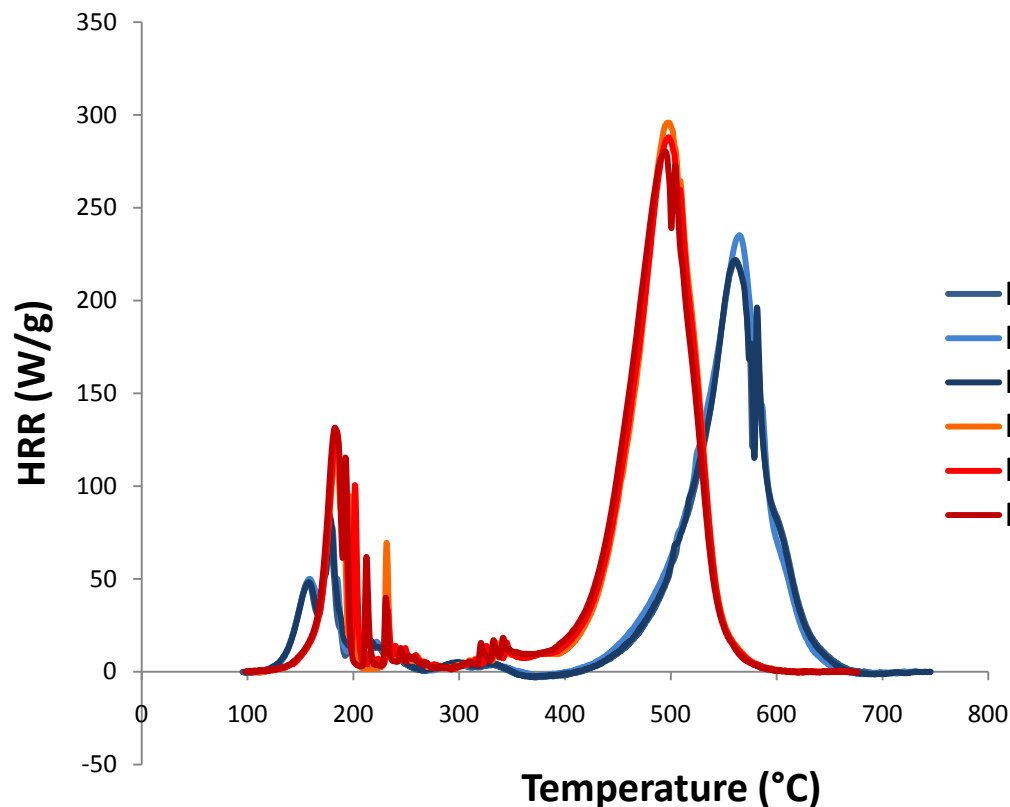
Cathode:  
**LiCoO<sub>2</sub>**  
Anode:  
**Synthetic Graphite**

Cycling Protocol:  
**1 mA between**  
**4.2 and 2.8 V**  
**C/5 Rate**



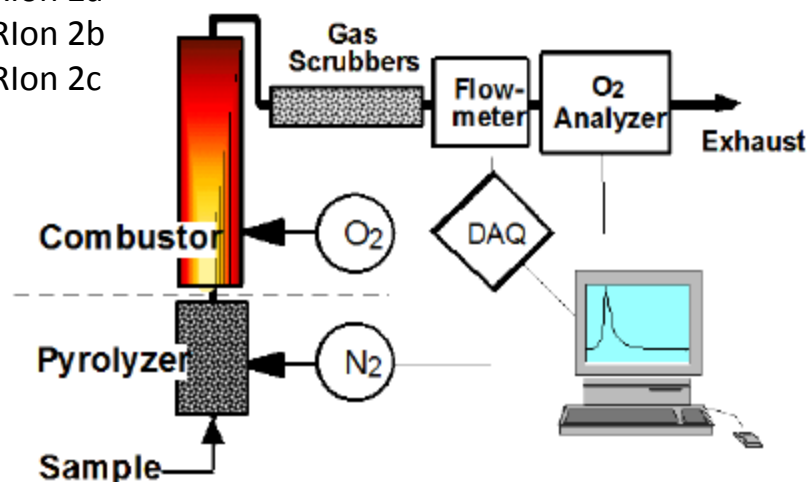
# Flammability Testing

## Pyrolysis Combustion Flow Calorimetry

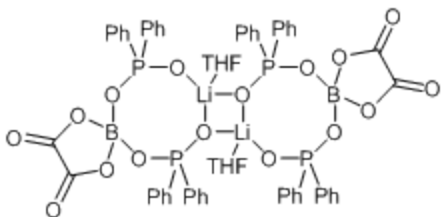
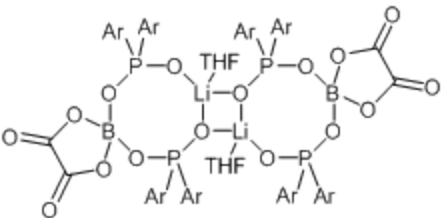
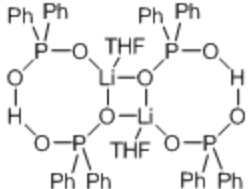


FRlon 1 Ar = Ph

FRlon 2 Ar = 2-MePh



# Flammability Testing

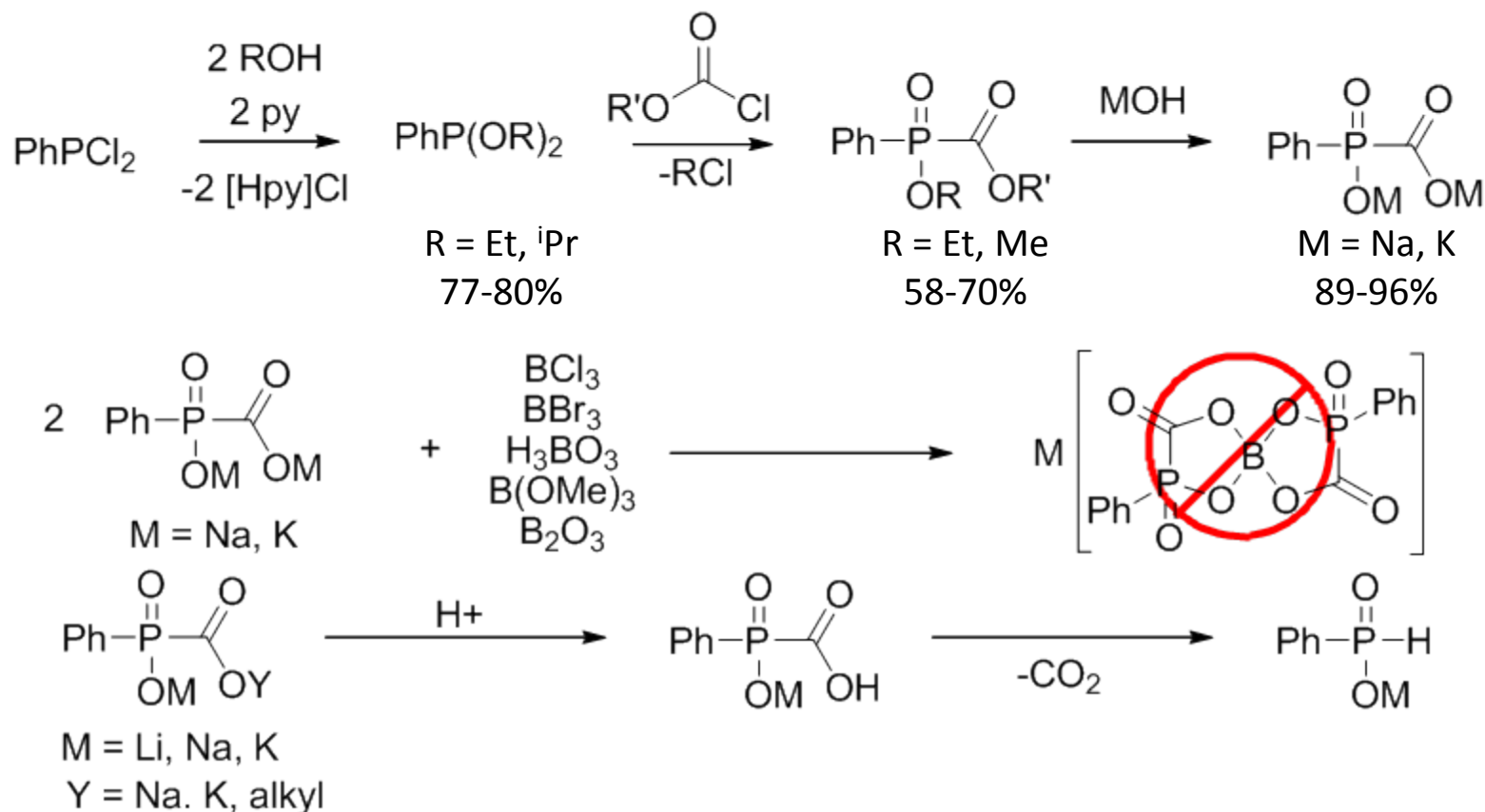
Sample	Char Yield <sup>a</sup> (wt%)	Mean HRR Peaks <sup>a,b</sup> (W/g)	Mean Max T <sup>a</sup> (°C)	Mean Total Hr <sup>a,c</sup> (kJ/g)
	23.62(0.3)	49(0.8) 82(2) 5(0.4) <b>225(6)</b>	158(0.7) 178(0.8) 298(2) <b>562(2)</b>	20.5(0.3)
	20.15(0.4)	125(6) 55(10) 15(3) <b>287(6)</b>	184(0.8) 231(0.4) 336(3) <b>497(1)</b>	24.7(0.1)
* 	7.93(0.2)	26(1) 177(2) 143(6) 150(38) 115(9) 113(2) 109(8)	99(1) 152(0.4) 402(3) 445(3) 523(3) 643(1) 721(3)	23.5(0.2)

<sup>a</sup>Standard Deviation in parentheses. <sup>b</sup>HRR = Heat Release Rate. <sup>c</sup>Total HR = Total Heat Release

\*This compound (not containing boron) provided for comparative purposes.

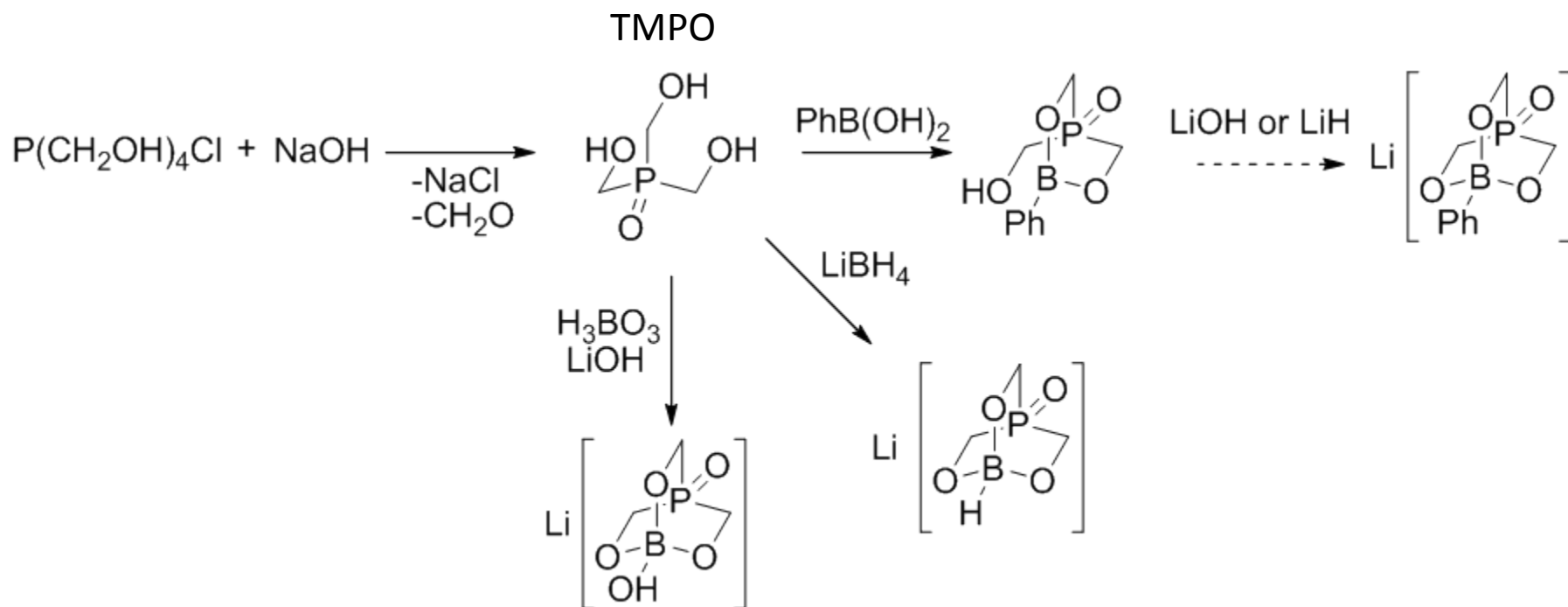
Data collected by Dr. Alexander Morgan at **University of Dayton**, Dayton, OH

# Synthesis of Anion Precursors



Upon addition of various boron reagents to the different salt precursors, decomposition was observed immediately, even at low temperatures. The decomposition product, phenylphosphinic acid, is formed via loss of CO<sub>2</sub>.

# Synthesis & Reactivity of TMPO

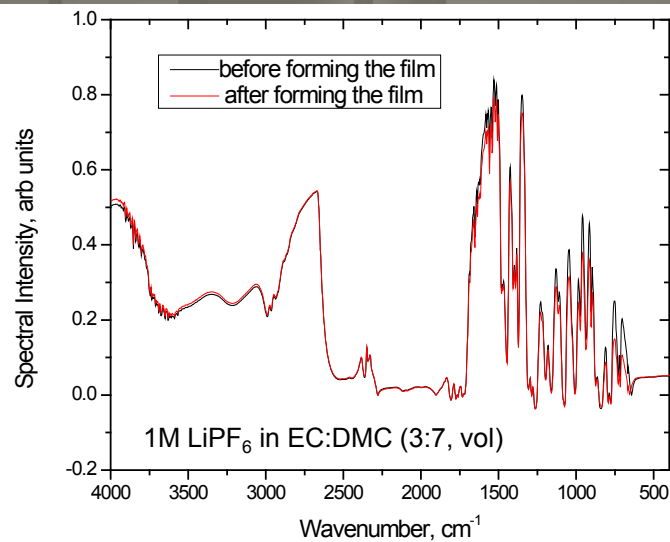
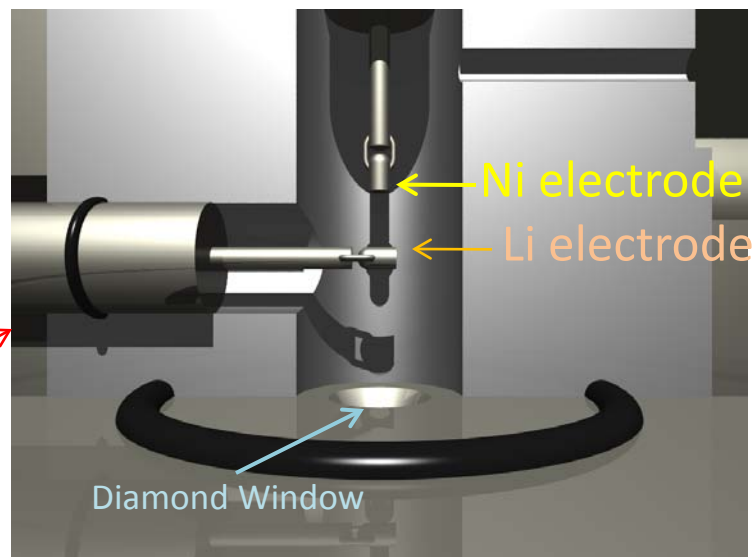


When tris(hydroxymethyl)phosphine oxide (TMPO) was reacted with phenyl boronic acid under the same reaction conditions as the carbon analog, no reaction was observed. TMPO is insoluble in toluene and a change in solvent has facilitated the formation of the TMPO-borate ester. Lithiation of the ester is currently being undertaken. Other boron starting materials are also being investigated for their reactivity with TMPO.

# *In situ* ATR-FTIR



Cell designed and built at CWRU for  
in situ ATR-FTIR measurement  
using a diamond window



# Proposed Future Work

- Continue design, synthesis, purification and characterization of FRLons and other safety enhancing bifunctional materials aimed at building knowledge base toward the rational search of materials that will enhance abuse tolerance without affecting adversely overall battery performance.
- Build new chemical platforms for FRLons.
- Engage other partners to further characterize FRLons, especially other BATT contractors.
- Develop procedures for large scale, economical syntheses of FRLons.
- Refine ATR-FTIR set up to improve sensitivity.

# Summary

1<sup>st</sup> and 2<sup>nd</sup> generation FRLons,  $\text{Li}[(\text{C}_2\text{O}_4)\text{B}(\text{O}_2\text{PAr}_2)_2]$ , were successfully synthesized from inexpensive, commercially available substrates and characterized using a wide array of techniques.

$\text{Li}[(\text{C}_2\text{O}_4)\text{B}(\text{O}_2\text{PPh}_2)_2]$  was shown to have excellent thermal stability in both the solid state and in solution.

$\text{Li}[(\text{C}_2\text{O}_4)\text{B}(\text{O}_2\text{PPh}_2)_2]$  shows no detrimental effects in coin cell testing studies.

The 1<sup>st</sup> and 2<sup>nd</sup> generation of FRLons shows very high char yields.

The synthesis of cyclic borate-phosphine oxides, another platform for FRLons, is currently being pursued.

A unique spectroelectrochemical cell was designed, constructed, and tested for performing *in situ* ATR-FTIR measurements of lithium ion anodes.



# Collaborations with Other Institutions

- i. Novolyte Technologies of Independence, OH will conduct coin cell tests using materials developed under this program in combination with their specialty chemicals. This company is outside the VT program.
- ii. Dr. Alexander Morgan of the Dayton University Research Institute in Dayton, OH, will determine the inherent flammability of materials developed under this program by combustion calorimetry using their unique microscale instrument. This organization is outside the VT program.
- iii. Dr. Robert Lattimer at Lubrizol Corporation will obtain TGA/MS data, which will enable a better understanding of the thermal decomposition patterns of the FRlons. This organization is outside the VT program.